

Hybrid Nanocomposite Membranes of Poly(vinyl alcohol) and Cerium Oxide for Pervaporation Dehydration of Ethanol at their Azeotropic Point \diamond

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RESEARCH ARTICLE

ABSTRACT: The study reports on the development of hybrid nanocomposite membranes of poly(vinyl alcohol) (PVA) loaded with metal oxide of cerium oxide (CeO_2) nanoparticles in different compositions from 1 to 10 wt. % that are used for pervaporation (PV) dehydration of ethanol at azeotropic point from aqueous mixtures i.e. 4.1 wt. % at 30°C. The PV performance of hybrid nanocomposite membranes were much superior to that of pristine PVA membrane in terms of selectivity and flux due to increased hydrophilicity of PVA membrane in the presence of nanoparticles. The membranes were crosslinked with tetraethylortho silicate (TEOS). Morphology of the membranes was assessed by scanning electron microscopy (SEM). It is observed that flux and selectivity increased analytically with increasing amount of nano CeO_2 particles in the PVA matrix. In case of hybrid adsorbent membrane containing 10 wt. % CeO_2 , selectivity for water was 1821 and flux 0.567 kg/cm² h that was attributed to the combined effects of molecular adhesion between particle surfaces and PVA matrix as well as higher selectivity of the adsorptive membrane as compared to plain PVA membrane.

KEYWORDS: pervaporation; poly(vinyl alcohol); nanocomposite membrane; metal oxide nanoparticles

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1. INTRODUCTION

In the pervaporation process a liquid feed stream is first pre-heated to operating temperature and then routed to a membrane module. The permeate transported through the membrane is vaporized on the permeate side of the membrane and heat is dissipated from the feed. As the partial pressure of the transported component, and with it the driving force for mass transportation, decreases at declining temperature, and the feed mixture has to be re-heated. In most cases, re-heating takes place outside the modules in separate heat exchangers [1-2]. Therefore for larger plants and high permeate rates, it may be necessary to provide for a very large number of small membrane modules with upstream heat exchangers. The vaporous permeate leaving the membrane module is condensed in an external heat exchanger. The vacuum pump is only used for the removal of the inert gases, but has no other function in the process.

Pervaporation (PV) separation has been the widely used method for separating aqueous-organic azeotropes [2-4]. In this method, chemical structure and physical nature of dense membranes have an effect on membrane performance and recent research efforts are moving towards developing mixed adsorbent membranes to obtain better mechanical strength and separation performance over plain polymeric

membranes. In the prior literature, several hybrid adsorbent membranes loaded with inorganic zeolite particles have been developed and used for dehydrating organics [2,5]. Separation using nanoparticles filled PV membranes occurs by adsorption-desorption and increased surface area due to nano filler effects due to the presence of small particles.

In continuation of the previous research work on aqueous-organic mixture separation the author tried to focus on the effect of nanoparticles in the polymer moiety. The present research work aimed to improve the separation factor along with flux and the role of the nanoparticles in the separation aspects.

2. EXPERIMENTAL

2.1 Materials and methods

Poly(vinyl alcohol) of reagent grade sample was all from Aldrich Chemicals Ltd., USA. Tetra ethyl orthosilicate (98 % pure) was purchased from Acros Organics, India, EPRUI Nanoparticles and Microspheres Co, Nanjing, China and hydrochloric acid was procured from s.d fine, India.

2.2 Particle size measurement of CeO_2

Particle size was measured by Zetasizer (Model 3000HS, Malvern, U.K). The sizes of the completely

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dried nano CeO_2 particles were measured by wet sample technique using wet sample adapter. Particles were dispersed in water and placed on sample corvette and zeta average diameter was recorded.

2.3 Membrane fabrication

Preparation of Nanocomposite membrane

PVA (5 g) was dissolved in 80 mL of deaerated distilled water at 60°C ; to this a known amount of TEOS was added along with 1 mL of HCl as a catalyst. The whole mixture was stirred overnight at 60°C to complete the reaction. The proper amounts of CeO_2 nanoparticles (to form 2.5, 5, 7.5, and 10 wt % of CeO_2 loading films) were first dried in a vacuum oven at 250°C and added to prepared PVA solution. The whole mixture was stirred for about 24 h to obtain the homogeneous solution, which was casted as membranes of uniform thickness. The dried membranes were peeled off from the glass plate. The hybrid adsorbent membranes are designated as CeO_2 -PVA-1, CeO_2 -PVA-2.5, CeO_2 -PVA-5, CeO_2 -PVA-7.5 and CeO_2 -PVA-10 that contained 2.5, 5, 7.5 and 10 wt % of CeO_2 nanoparticles respectively.

2.4 Pervaporation experiments

PV experiments were performed on 100 mL batch level with an indigenously constructed glass manifold operated at vacuum level of 0.05 mmHg in the permeate line. The effective membrane area was 20 cm^2 and weight of the feed mixture taken in the PV cell was 70 g. Weight of permeate collected was measured using Mettler Balance (model B 204-S, Greifensee, Switzerland: accuracy 10^{-4} g) to determine flux, J ($\text{kg.m}^{-2}\text{h}^{-1}$) using weight of liquids permeated, W (kg), effective membrane area, A (m^2) and measurement time, t (h) as:

$$J = \frac{W}{At} \quad (1)$$

The analysis of feed and permeate samples was done using Nucon Gas Chromatograph (model 5765, Mumbai, India) equipped with a Thermal Conductivity Detector (TCD) and DEGS or Tenax packed column of 1/8" ID of 2 m in length. Calibration factors were fed into GC software to obtain the analysis for unknown samples. The selectivity, α and separation index, PSI , were calculated as:

$$\alpha = \left(\frac{P_A}{1 - P_A} \right) \left(\frac{1 - F_A}{F_A} \right) \quad (2)$$

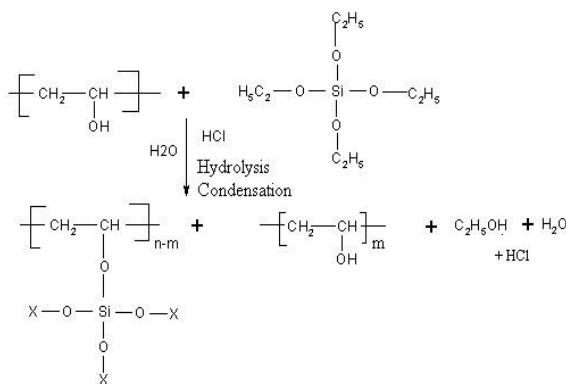
$$PSI = J (\alpha - 1) \quad (3)$$

where F_A is weight % of water in feed and P_A is weight % of water in permeate. A minimum of three independent readings on flux and α were taken under similar conditions of temperature and feed compositions to confirm steady-state pervaporation.

3. RESULTS AND DISCUSSION

3.1 Reaction of PVA and TEOS

The crosslinking reaction between PVA and TEOS are shown in Scheme 1. Polycondensation reaction was carried out as per the procedure reported earlier [1-2]. While preparing PVA/TEOS hybrid matrix membranes, TEOS was hydrolyzed in the presence of an acid catalyst (HCl) producing the silanol groups.



Scheme 1 Reaction scheme of poly(vinyl alcohol) and tetraethoxysilane.

3.2 Scanning Electron Microscopy

SEM image of the surfaced of the hybrid membranes shown in figure 1, containing plain and 5 Wt. % of nano CeO_2 loaded PVA hybrid membranes as shown in Figure 2. Notice that particles of CeO_2 are distributed uniformly at the molecular level in PVA polymer matrix.

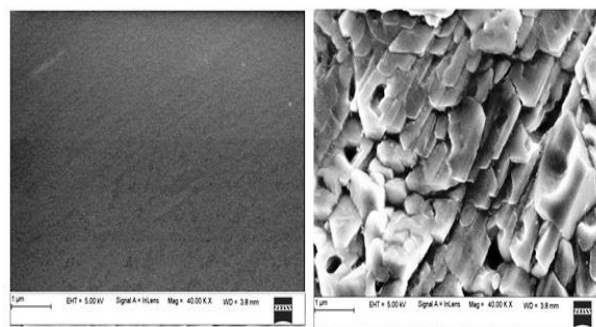


Figure 1. (a) Plain and (b) Nano CeO_2 embedded PVA membrane.

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3.3 Particle size and distribution

The particle size distribution of a material can be important in understanding its physical as well as chemical properties of the material. The histogram of particle size distribution is shown in Fig. 2. CeO₂ nanoparticle varies in the size between 20 and 30 nm. SEM picture of the membrane displayed in Fig. 3 indicates the homogeneous distribution of particles in the matrix.

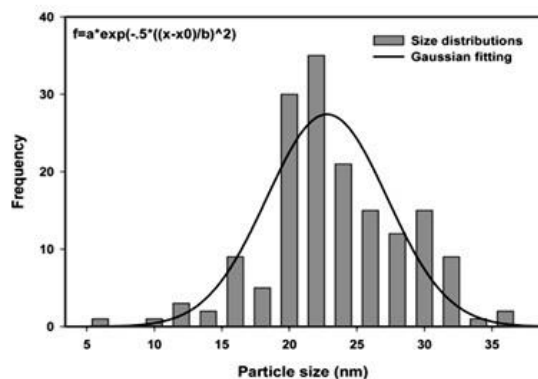


Figure 2. Zeta sizer Histogram of the particle size distribution.

3.4 Membrane Performance

Incorporation of CeO₂ nanoparticles as a nano material into PVA matrix resulted in the formation of dense homogeneous membranes those are quite stable enough upon standing at ambient temperature up to a month or even more. The nano metal oxide-incorporated membranes have been tested for sorption studies in water-ethanol mixtures at their azeotropic point viz., 95.9: 4.1 water: ethanol mixture to check their suitability in PV experiment.

The presence of CeO₂ nanoparticles into PVA matrix would increase the free water channels to facilitate transport of large number of water molecules through the mixed matrix membranes than with the plain PVA membrane. The results are tabulated in the Table-I. Both flux and selectivity values of PVA adsorbent membranes increase with increasing amount of CeO₂ nanoparticles, indicating an increased hydrophilicity of the hybrid adsorbent membranes due to the presence of CeO₂ nanoparticles. Notice that the extent of water extracted on the permeate side of the membrane increases systematically with increasing amount of filler loading. The highest result was obtained by 10 wt % CeO₂ nanoparticle loaded PVA membrane matrix was performed. This is due to the enhanced surface area due to the nanoparticles and polymeric chain stiffness was improved due to the addition of TEOS.

Table 1

Membrane	Water (wt. %)		Flux (kg/m ² h)	Selectivity (α)
	Feed	Permeate		
Plain PVA	4.2	69.2	0.143	51.2
PVA + 2.5 wt.% CeO ₂	4.1	95.0	0.228	456
PVA + 5 wt.% CeO ₂	4.0	97.2	0.349	804
PVA + 7.5 wt.% CeO ₂	4.3	97.4	0.364	1067
PVA + 10 wt.% CeO ₂	3.2	97.7	0.567	1321

4. CONCLUSION

To improve membrane performance, one can generally follow two distinct strategies, i.e., either to synthesize new polymers with specific chemical architectures or to modify the existing polymers by incorporating suitable fillers. This paper reports results obtained according to the latter route. It is realized from the literature that fillers like metal oxide nanoparticles can improve separation properties of membranes, provided that appropriate zeolite and polymer combinations are chosen. The CeO₂ nanoparticles filled PVA hybrid adsorbent membranes of this study had not been previously reported in the literature. The hybrid adsorbent membranes studied here were effective in PV dehydration of ethanol at its azeotropic point with water. The addition of even a small amount of CeO₂ nanoparticles into PVA membranes has improved both flux and selectivity to water over that of the plain PVA membrane.

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